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An investigation of the parameters effecting the agglomerate size of a PZT ceramic powder prepared with a sol–gel technique

S. Linardos, Q. Zhang, J.R. Alcock*

School of Industrial and Manufacturing Science, Cranfield University, Bedfordshire MK43 0AL, UK

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Abstract

This paper describes the production of $Pb_{1.0}Zr_{0.9}Ti_{0.1}O_3$ ceramic powder, by using metal organic precursors as starting materials and a polyvinylpyrrolidone (PVP) as an agglomeration control agent. In this study, the effects of water content, aging time and polyvinylpyrrolidone molecular weight on the agglomeration behaviour of the powders were investigated. Least agglomerated powder, with size population ranges 60–200 nm and 200–800 nm, was produced from gel which contained the lower molecular weight of polymer and was unhydrolysed and unaged.

Keywords: Powders-chemical preparation; Sol–gel processes; PZT; Agglomerate

1. Introduction

Sol–gel techniques can produce fine mean particle size powders with narrow particle size distributions. In powders designed for sintering this can lead to a high Gibb's free energy per unit surface area and hence a low required sintering temperature. However, for this goal to be achieved the agglomeration behaviour of the fine particle-size ceramic powder must be carefully controlled.

Processing routes for producing monodispersed fine powders are becoming increasingly common. Sol–gel techniques have previously been used by several authors[1–7] to create PZT powders.

In a previous paper,[8] a new sol–gel route, was used to prepare PZT sub-micron powder. This utilised polyvinylpyrrolidone (PVP), which appeared to have little effect on the primary particle size of the PZT but to strongly affect the agglomerate size when added in a second process stage.

In this paper, agglomeration control in this sol–gel route was studied. The effects of water content, aging time and polyvinylpyrrolidone molecular weight were investigated.

2. Experimental

The preparation route of the $Pb_{1.0}Zr_{0.9}Ti_{0.1}O_3$ powder is shown in Fig. 1.

To produce 320 ml of sol, the following route was used. 12.14 g of lead(II) acetate trihydrate was left under vacuum at 100 °C for 24 h to remove the water. 12.21 g of zirconium(IV) propoxide, 76.33% by weight in *n*-propanol and 0.9 g of titanium(IV) isopropoxide were dissolved in 240 ml isopropanol. This mixture was heated to 80 °C under stirring. After 3 h the lead(II) acetate was added. The mixture was stirred for another 3 h under the same conditions. Extra isopropanol was added until the final volume of the solution reached the 320 ml. A light-transparent PZT sol was obtained. To transform this into a PZT-PVP sol, 10.42 g of polyvinylpyrrolidone with average molecular weight of 10,000 were added and the stirring was continued until the mixture became clear yellow in colour.

The resulting PZT-PVP sol had a concentration of 0.1 M of lead. The $Pb(OAc)_2$: PVP weight ratio of the sol was 1:1.

The sol was subsequently treated to a secondary stage designed to investigate agglomerate formation in the subsequent powder.

The experimental variables of the second stage and their levels are tabulated in Table 1. The variables were: quantity of water, PVP molecular weight and aging time.

Each powder was prepared from 20 ml of sol and each PZT-PVP gel was left for 20 min under stirring at 700 rpm. For the

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* Corresponding author. Fax: +44 1234 752473.
E-mail addresses: ranil_spy@yahoo.com (S. Linardos), j.r.alcock@cranfield.ac.uk (J.R. Alcock).

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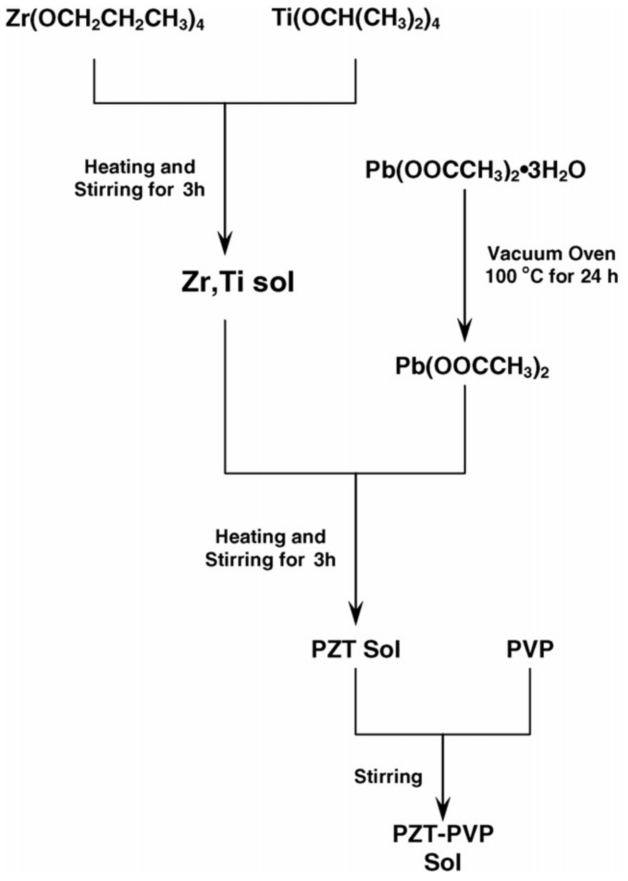


Fig. 1. Preparation route of PZT-PVP sol.

Table 1
The experimental variables and their levels

Variable	Levels per 20 ml of sol	
[Pb]:[H_2O] moral ratio	[1]:[0]	[1]:[30]
Polymer MW	10000	1300000
Aging time (days)	0	5

sols with water added, water was first diluted in 10 ml of isopropanol and then added to 20 ml of sol to hydrolyse it. The [Pb]:[H_2O] molar ratio of the sol was [1]:[30]. A selection of the gels was then aged for 5 days. The powders were subsequently heat treated at 500 °C for 24 h to obtain crystalline PZT.

A Philips XL series scanning electron microscope (SEM) was used for powder imaging. Size measurements of the powder were performed using a Zeta-Sizer 3000 (Malvern Instruments). Each powder before the measurements was diluted in water and left in an ultrasound bath for 40 min. The Zeta-Sizer was calibrated for the analysis step to have an upper determination limit of approximately 5 μm.

3. Results

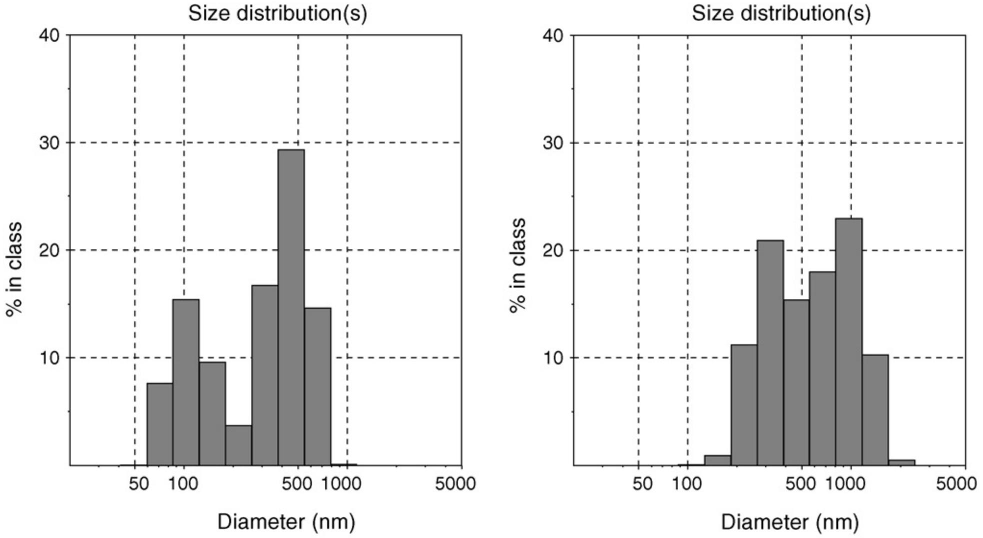
Figs. 2 and 3 show the agglomerate size distributions of PZT powders that were produced in this study. A summary table of their agglomerate size distributions is given in Table 2.

Fig. 2 presents the agglomerate size distributions of PZT powders that were produced from an unhydrolysed gel. Fig. 2a shows the agglomerate size distribution from the unaged sample with second stage PVP with 10,000 MW. A bimodal agglomerate size distribution was present, with agglomerate size population ranges 60–200 nm and 200–800 nm. Fig. 2b shows the measured agglomerate size range for the aged sample with the same molecular weight of PVP. This was 200–2000 nm. Fig. 2c shows the agglomerate size distribution for the unhydrolysed powder with second stage PVP with 1,300,000 MW. The measured particle size range was 80–5000 nm for the unaged sample, where 5 000 nm represents the upper measurement limit of the measuring device. For the aged sample, Fig. 2d, the agglomerate size range was 700–5000 nm.

Fig. 3 shows PZT powders that were produced from a hydrolysed gel. Fig. 3a shows the measured agglomerate size for the sample with second stage polymer of 10,000 MW. This was bimodal, with populations in the range of 100–400 nm and 400–5000 nm. For the aged sample with the same PVP molecular weight, Fig. 3b, the measured agglomerate size range was 900–5000 nm. For the powders with 1,300,000 MW second stage PVP the measured agglomerate population range was

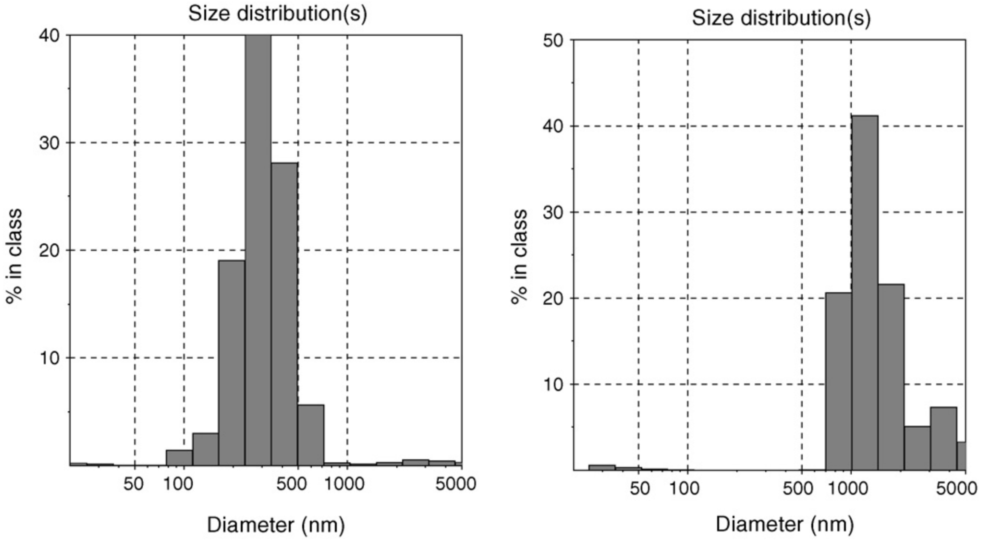
Table 2
Experimental conditions, agglomerate size range and peak agglomerate size for the powders with 6 g of second stage PVP

Water	Molecular weight	Aging (days)	Range (nm)	Peak size range (nm)	Quantity (volume %)	Figure
No	10000	0	60–800 (bimodal)	90–110 400–600	16 29	4a
No	10000	5	110–2100 (bimodal)	400–500 800–1100	21 23	4b
No	1300000	0	80–5000	210–320	40	6a
No	1300000	5	700–5000	1000–1400	41	6b
Yes	10000	0	50–4000 (bimodal)	120–140 800–1000	10 23	8b
Yes	10000	5	900–5000	1800–2600	37	8b
Yes	1300000	0	70–2800	600–800	18	10b
Yes	1300000	5	900–4000	2000–3000	38	10b



(a) **20 ml of sol, 10 000 MW of PVP, No water**

(b) **20 ml of sol, 10 000 MW of PVP, No water Aged for 5 days**



(c) **20 ml of sol, 1300 000 MW, No water**

(d) **20 ml of sol, 1300 000 MW, No water, Aged for 5 days**

Fig. 2. Size distribution in volume diagrams of PZT powders produced from unhydrolysed gel for different polymer molecular weight and aged time.

70–3000 nm for the unaged sample, as shown in Fig. 3c, and 600–4000 nm for the aged sample, as shown in Fig. 3d.

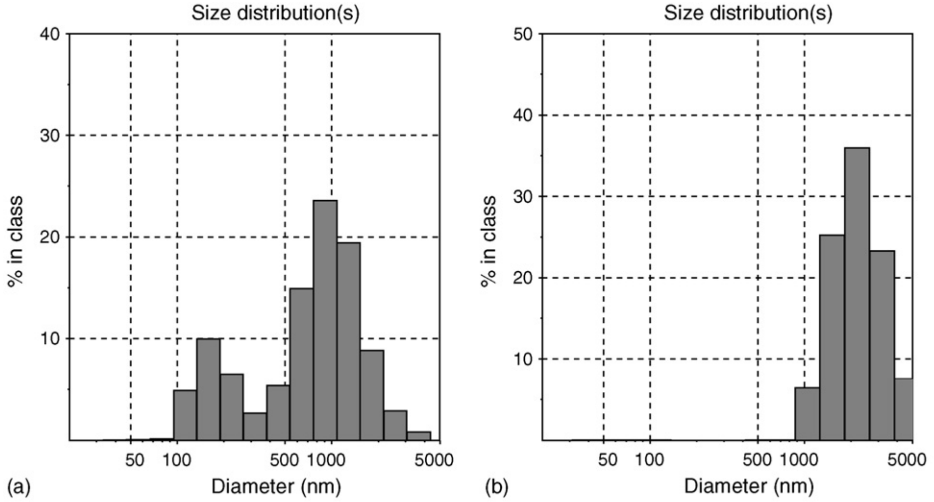
Fig. 4 are SEM micrographs of PZT powders that were produced under different conditions. No noticeable differences can be observed in the primary free standing particles which size is between 50 and 100 nm.

4. Discussion

This processing study appears to confirm the observation made during the initial work on this processing route[8] that the second stage processing route variables have little effect on the primary particle size.

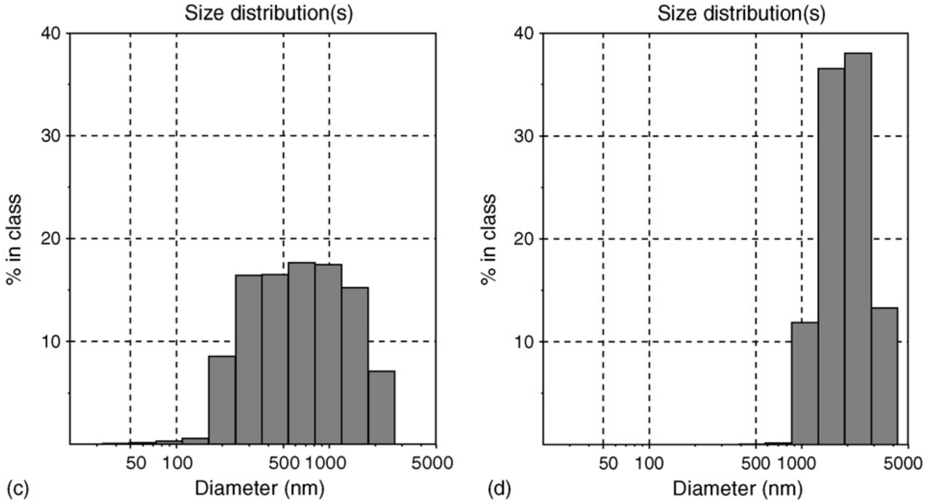
A comparison between the size measurements of the samples that were aged for 5 days and the unaged samples, Figs. 2 and 3 show that the average size of the agglomerates increased with time. For example, the unaged sample in Fig. 2a had a bimodal agglomerate size population with ranges 60–200 nm and 200–700 nm. The aged sample in Fig. 2b had particle size range 200–2000 nm. Similar comparisons can be made between the other samples. During the aged period the particles would have had more time to react and create bigger agglomerates in the solution.[9,10]

A comparison between the size measurements of the samples with similar preparation conditions (water amount, aged time) but different molecular weight of polymer shows that smaller peak size ranges of agglomerates were produced when the polymer with 10,000 average molecular weight was used. For example, the sample with 10,000 average MW of polymer, in Fig. 2a, had agglomerate size populations with ranges 60–200 nm (30% in volume of the particles belonged to this range) and 200–700 nm (70% in volume of the particles



20 ml of sol, 10 000 MW of PVP, [Pb]:[H O] molar ratio [1]:[30] in the sample

20 ml of sol, 10 000 MW of PVP, [Pb]:[H_2O] molar ratio [1]:[30] in the sample, Aged for 5 days



20 ml of sol, 1300 000 MW of PVP, [Pb]:[H_2O] molar ratio [1]:[30] in the sample

20 ml of sol, 1300 000 MW of PVP, [Pb]:[H_2O] molar ratio [1]:[30] in the sample, Aged for 5 days

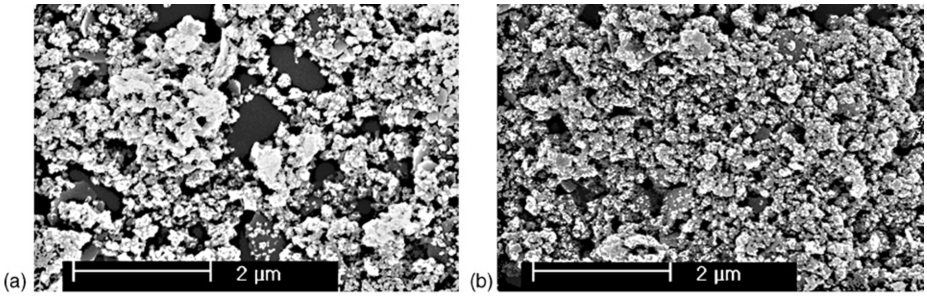
Fig. 3. Size distribution in volume diagrams of PZT powders produced from hydrolysed gel for different polymer molecular weight and aged time.

belonged to this range). The sample with 1,300,000 average molecular weight, in Fig. 2c, had agglomerate size population with ranges 80–700 nm (95% in volume of the particles belonged to the 200–700 nm range) and 2000–5000 nm. This indicated that the polymer with the smaller molecular weight interacted more efficiently with the sol and better protected the colloidal particles from coming into contact and, hence, create bigger agglomerates.

The effect of different molecular weight of PVP on the particle size has also been demonstrated by Busser et al.[11] Busser et al. estimated that a 4.5 nm spherical rhodium (Rh) particle in a water base Rh^+-PVP solution with molecular weight of the polymer 40,000 is surrounded by 192 polymer strings. The same particle in a similar solution with polymer molecular weight 360,000 will be surrounded by 21 strings. For a particle to obtain sufficient stabilisation a large fraction of the metal surface has to be surrounded by the polymer.[12] For this reason a low number of polymer strings per particle indicates that multiple adsorption of the polymer on the metal surface is necessary for sufficient stabilisation.

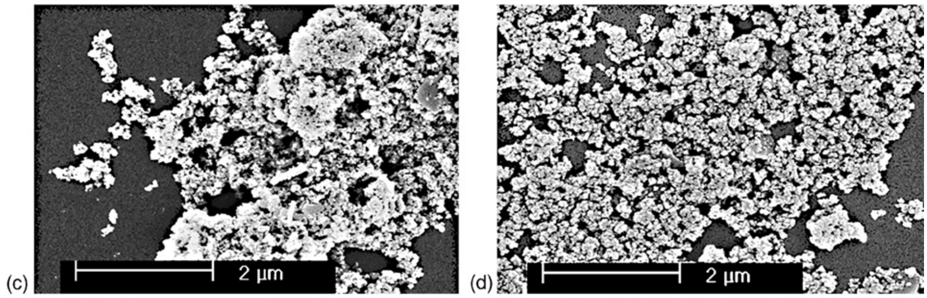
A comparison between the size measurements of the samples with similar preparation conditions (polymer molecular weight, aging time) but different water amount shows that the unhydrolysed samples gave powders with smaller agglomerates. For example, Fig. 2a shows the unhydrolysed sample with bimodal agglomerate size population ranges 60–200 nm and 200–700 nm, whereas Fig. 3a shows the hydrolysed sample with bimodal particle size population in the range 100–400 nm and 400–5 000 nm. When hydrolysis occurs in a sol, condensation reactions also occur. This leads the smaller particles to react and create more complex and larger structures.[13]

The combination of the conditions that gave the finest powder was that of 10,000 molecular weight PVP, where the sample



(a) 20 ml of sol, 10 000 MW of PVP, No water

(b) 20 ml of sol, 10 000 MW of PVP, No water Aged for 5 days



(c) 20 ml of sol, 1300 000 MW of PVP, [Pb]:[H_2O] molar ratio [1]:[30] in the sample

(d) 20 ml of sol, 1300 000 MW of PVP, [Pb]:[H_2O] molar ratio [1]:[30] in the sample, Aged for 5 days

Fig. 4. SEM micrographs of PZT powders for different water amount, polymer molecular weight and aged time.

was unhydrolysed and unaged, for which the agglomerate size distribution is given in Fig. 2a.

5. Conclusions

In this paper agglomeration control of a sol–gel route for the production of PZT powder was studied.

Agglomeration control was achieved by the addition of polyvinylpyrrolidone during a second processing step. The primary particle size appeared to be unaffected by the changing the process variables during this second stage.

Unhyrdolysed PVP containing gels produced smaller average agglomerate sizes, as did unaged PVP containing gels. The effect of PVP molecular weight was less clear cut, but a lower molecular weight of PVP appeared to reduce agglomerate size for powder produced from an unhyrdolysed gel.

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